ANNUAL PROJECT REPORT
AS OF DECEMBER 1999

1. PROJECT SPONSOR:
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3. OCDO GRANT NO: OCRC/98-A4.11

4. PROJECT UPDATE ✔ OR FINAL REPORT

5. PROJECT TITLE: Simultaneous selective catalytic reduction of NO and SO_2 using CH_4 over supported palladium catalysts

6. PROJECT TERM: FROM: September 1, 1998 TO: August 31, 1999

7. PROJECT CO-SPONSORS:

NAME	COST SHARE
OCDO	$ 74,994
OSU	$29,429
TOTAL PROJECT COST:	$104,423

I. ABSTRACT

8. OBJECTIVES:

While the large coal reserves of the state of Ohio makes increasing reliance on coal utilization a necessity, the growing concern about its impact on the environment renders development of new technologies that can minimize the negative effect even more urgent.

The main purpose of this project is to investigate hydrocarbon-based catalytic reduction of NO_X under stack gas conditions with methane as an alternative reducing agent. The main points to be addressed are the nature of the active sites, adsorption/ activation behavior of NO and CH_4, and the interaction between the two metals under reaction conditions over supported palladium catalysts paired with lanthanide metals. The resistance of the catalyst to SO_2 and H_2O in NO-CH_4 reduction reactions will also be examined. The studies which are aimed at acquiring a fundamental understanding of the catalytic and kinetic phenomena involved in these reactions will be coupled with experiments that examine the same reactions under stack gas conditions to develop a knowledge base which will lead the way to the design of catalytic systems that can be applied to NO_X emissions from coal -burning combustion sources.

9. WORK DONE AND CONCLUSIONS:

A Gd-Pd based catalyst was developed with capability to completely reduce NO to nitrogen (selectivity higher than 96%) in the presence of excess oxygen conditions. Moreover, the presence of 7% water in the feed did not affect the performance of the catalyst.

In the presence of 145 ppm SO_2 in the reactant mixture, the catalyst was able to reduce NO at over 70% efficiency for 6 hours.

The results from temperature programmed desorption experiments suggest that NO and CH_4 competitively adsorb on the similar sites. Preliminary results obtained from diffuse reflectance infrared Fourier Transform spectroscopy showed that some of NO adsorption sites form various types of nitrates while in the presence of both NO and CH_4, the decrease in the signal from nitrates and formation of N-H vibration band are observed. X-ray photoelectron spectroscopy showed the oxidation state of most Pd on active catalysts to be 0 while that of deactivated catalysts to be +2. These results indicate that the Pd^0 sites necessary for $NO+CH_4+O_2$ reaction.

10. PLANS FOR COMING YEAR:

The main objective of second year of this project is to modify the best working catalyst in order to increase its resistance to SO_2, and other stack gas components. In addition, the use of reducing agents other than methane will be investigated. That will be achieved by trying new supports, such as activated carbon, Al_2O_3 and ZrO_2. New promoters will also be introduced, such as alkaline and alkaline earth metals. These changes are expected to make our catalyst more competitive, in terms of cost and performance, with respect to the commercial catalysts used in ammonia-based NO SCR.

II. HIGHLIGHTS/ACCOMPLISHMENTS

The Gd-Pd supported over titania can effectively reduce NO using CH_4 as a reducing agent in the presence of excess oxygen and water with 100% NO conversion and over 96% selectivity to N_2. The tolerance toward oxidation in excess oxygen conditions and SO_2 poisoning of the catalyst was greatly enhanced over the Gd-Pd catalyst compared to the Pd-only catalysts that were studied previously in our laboratory. The characterization studies on the catalysts helped to understand the nature of active sites in various catalytic steps in NO-CH_4 reduction reaction.

III. ARTICLES/PRESENTATIONS

1. "Role of lanthanide elements on the catalytic behavior of supported Pd catalysts in the reduction of NO with methane", J. Mitome, E. Aceves, U.S. Ozkan, *Catalysis Today*, 53 (1999) 597.
2. "Selective NO reduction with CH_4 in the presence of SO_2, H_2O, and O_2 over Pd-based catalysts", J. Mitome, E. Aceves, U.S. Ozkan, Tri-State Catalysis Society Meeting, Poster presentation, Louisville, KY, April, 1999.
3. "Selective NO reduction with CH_4 in the presence of SO_2, H_2O, and O_2 over Pd-based catalysts: DRIFTS and Isotopic labeling studies", J. Mitome, E. Aceves, U.S. Ozkan, 16th North American Catalysis Society Meeting, Poster presentation, Boston, MA, June 1999.